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SUPPLEMENTAL ON-LINE MATERIAL, INFLUENCE OF pH ON PLUTONIUM DESORPTION/SOLUBILIZATION FROM SEDIMENT

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Supplemental On-Line Material

Influence of pH on Plutonium Desorption/Solubilization from Sediment

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Oxidation State Analysis Technique. The oxidation state distribution of Pu in each sample for each reaction time was measured using a combined ultrafiltration and solvent extraction technique (*1-4*). First the oxidation state distribution of aqueous Pu is measured. Then the total system (solid and aqueous phase combined) Pu oxidation state distribution is measured by lowering the pH to leach Pu from the solid phase.

For each reaction time, a 2.5-mL aliquot of the aqueous phase was removed and passed through a 12-nm filter (Microsep 30K MWCO Centrifugal Device; Pall Corporation, East Hills, NY). An aliquot of the filtrate was removed to determine the aqueous phase Pu concentration, and oxidation state distribution in the remaining filtrate was measured using the parallel solvent extraction technique discussed above. These data can be used to express the concentration and oxidation state distribution of Pu in the aqueous phase (Equation 1).

$$[Pu]_{aq} = [Pu(IV)]_{aq} + [Pu(V)]_{aq} + [Pu(VI)]_{aq} \qquad (1)$$

The pH of the remaining sample, aqueous and solid phase, was lowered to 1.5 using $HClO_4$ and mixed for 15 minutes to quantitatively leach Pu(V) and Pu(VI) from the mineral surface. Quantitative leaching of Pu(V) and Pu(VI) was verified using Np(V) and U(VI) as oxidation state analogs. Incomplete leaching of tetravalent actinides was quantified and accounted for in the determination of the Pu oxidation state distribution by assuming that any Pu remaining on the solid phase was Pu(IV). The Pu mass balance for the total system (solid and aqueous phases) is expressed in Equation 2:

$$\begin{aligned} m_{Total}^{Pu} &= [Pu(IV)]_{aq} V_{aq} + [Pu(IV)]_{solid}\, m_{solid} + [Pu(V)]_{aq} V_{aq} + [Pu(V)]_{solid}\, m_{solid} + \\ &+ [Pu(VI)]_{aq} V_{aq} + [Pu(VI)]_{solid}\, m_{solid} \qquad (2) \end{aligned}$$

where *m* is the mass of the solid phase (g), *V* is the volume of the aqueous phase (L), and [*Pu(IV)*], [*Pu(V)*], and [*Pu(VI)*] are the concentrations of Pu in the these oxidation states (mol/L or mol/g). Again, the $[Pu(X)]_{aq}$ parameters were measured in the aqueous phase in contact with the solid phase and $[Pu(X)]_{solid}$ parameters were measured in the filtered pH 1.5 extracts. The Pu distribution among the three oxidation states is expressed as a fraction to account for both the solid phase and aqueous phase contributions (Equation 3).

$$f_{aq+solid}^{Pu(Total)} = 1.0 = f_{aq+solid}^{Pu(IV)} + f_{aq+solid}^{Pu(V)} + f_{aq+solid}^{Pu(VI)} \qquad (3)$$

As an experimental control, single oxidation state Pu(IV), Pu(V), and Pu(VI) solutions remained as 98 ± 4% Pu(IV), 97 ± 4% Pu(V), and 98 ± 2% Pu(VI) after being carried through the ultra-filtration/ solvent extraction oxidation state analysis technique described above. The integrity of the initial oxidation state was maintained throughout the procedure, validating the stability of each oxidation state as well as the separation method in 0.01 M NaCl.

Validation of Oxidation State Analysis Procedure. Aliquots of ^{230}Th(IV), ^{237}Np(V), or ^{233}U(VI) were mixed with hausmannite and pyrolusite suspensions at pH 8 for one hour. Then the solutions were acidified and the actinides were leached for various times and passed through 12-nm filters. The concentration of the oxidation state analogues in the leachate was measured using liquid scintillation counting. It was found that a 15 minute leaching step was sufficient to obtain quantitative leaching of Np(V) and U(VI) from the solid phase. Quantitative leaching of Th(IV) was not achieved in 15 minutes. Therefore any Pu remaining on the solid phase following a 15 minute leaching step was assumed as Pu(IV).

Plutonium Sorption as a Function of pH:

Table S1. Apparent Solubility (mol L^{-1}) and Apparent Distribution Coefficients (K_d; mL/g) of Pu as a Function of pH.

pH	Pu(IV)–1 day		Pu(V)–1 day		Pu(V)–33 days		Desorption–24 yr	
	Solubility	K_d	Solubility	K_d	Solubility	K_d	Solubility	K_d
4	9.5e-8	25	1.3e-7	5	4.3e-10	58,000	2.3e-8	1570
5	7.5e-8	38	7.5e-8	24	3.3e-10	80,000	3.6e-9	10,200
6	3.2e-9	1330	9.2e-9	341	8.3e-11	342,000	7.5e-10	49,500
7	1.1e-9	3930	7.5e-10	4430	4.2e-11	687,000	1.2e-10	346,000
8	6.6e-10	6400	5.6e-10	5740	NA	NA	2.3e-11	1,639,000

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